

PATENT SPECIFICATION

723 149



Date of Application and filing Complete Specification: May 28, 1952.

No. 13607/52.

Application made in United States of America on June 19, 1951.

Application made in United States of America on June 29, 1951.

Complete Specification Published: Feb. 2, 1955.

Index at acceptance:—Classes 1(1), F3(A1A: B2A); and 32, E(1: 2).

COMPLETE SPECIFICATION

Cracking Heavy Hydrocarbons

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention is concerned with a combination process wherein a heavy hydrocarbon feed, such as a heavy petroleum residual oil, is thermally cracked into lighter fractions in the presence of inert solid particles and such product lighter fractions are then up-graded by a catalytic conversion treatment such as cracking.

Various processes have already been proposed for converting hydrocarbons by first removing catalyst-contaminating constituents in a coking step and, usually after intervening condensation and fractionation in pipe stills where coke-forming bottoms were separated, cracking the resulting product in the presence of a fluidized catalyst. However, such processes were often characterised by the production of gasoline of undesirably low quality during coking; and by the formation of coke deposit in fractionation zones and elsewhere. Difficulties have also been encountered in attempting to utilize in the process the heat liberated during catalyst regeneration. Furthermore in some designs, especially where no extraneous condensation and fractionation was provided for between the coking and cracking stages, there is a tendency to excessive contamination of catalyst by coke in the second reaction stage.

In accordance with the present invention, there is provided a method of converting a heavy hydrocarbon feed, such as a heavy petroleum residual oil, into lighter fractions which comprises subjecting said feed to a thermal cracking and coking treatment in a first reaction zone in the presence of inert

finely divided solids, passing the product vapors from said first reaction zone through a scrubbing zone in which they are scrubbed by a liquid hydrocarbon oil which serves to condense and retain in the scrubbing zone the higher boiling constituents of said product vapors and any finely divided solids entrained therein, passing the vaporous effluent from the scrubbing zone to a second reaction zone wherein said vaporous effluent is subjected to a catalytic up-grading treatment in the presence of catalytically active solids, and removing up-graded hydrocarbon vapors from said catalytic conversion zone.

Preferably the second reaction zone is located vertically above the first reaction zone with the scrubbing zone interposed therebetween. Both reactions zones are preferably operated with finely divided solids maintained in the form of fluidized beds in the respective zones.

The scrubbing zone employed in the method of the invention preferably comprises a pool of relatively cool hydrocarbon oil through which the vapors leaving the first reaction zone are passed before being passed to the second reaction zone. Such pool of relatively cool oil serves to condense the higher boiling constituents of the vapor and at the same time forms a filter to retain any solid particles entrained in the said vapors before passing to the second reaction zone. If desired, the gases leaving the first reaction zone may be passed through a gas solids separator to remove the solids before passing to the condensation zone. The temperature of the pool of oil in the scrubbing zone may be maintained at the desired level by continuously withdrawing part of the oil or slurry therein and cooling it prior to recycling it to the scrubbing zone. Alternatively the pool in the scrubbing zone may be cooled by continuous addition of cool make-up hydrocarbon oil.

As will be appreciated build-up of liquid will occur in the scrubbing zone due to condensation and it is preferred to remove oil or

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- slurry from the scrubbing zone and pass it, with or without cooling and with or without removal of the solid material, to the first reaction zone.
- 5 A second scrubbing zone may also be provided above the first scrubbing zone to effect further condensation of high boiling constituents from the first reaction zone. This second partial condensation zone preferably likewise comprises a pool of hydrocarbon oil which may be constituted by a relatively cool portion of the hydrocarbon feed to the first reaction zone. The temperature of said second condensation zone will be lower than that in the 10 said first condensation zone, the temperature of the latter being preferably 100 to 200° F. below that of the first reaction zone. Liquid hydrocarbon oil, including condensed high boiling constituents, may be continuously 15 withdrawn from the second condensation zone and supplied as make-up oil to the said first condensation zone.
- The invention is broadly applicable to dual-zone conversion of whole or reduced crude petroleum stocks containing heavy components as well as cycle stocks having a boiling range above about 900 to 1150° F. (atmospheric equivalent) and a gravity of 20° API or lower, 20 and even to lighter stocks such as gas oils. The importance of the invention lies in the fact that it permits ready control of end boiling point of the vapors fed from the first coking zone directly to the second for example catalytic cracking zone. Solid coke as well as feed fractions having strong coke forming tendencies are 25 kept out of the second or catalytic cracking zone by intimate scrubbing with a liquid hydrocarbon maintained at the desired temperature in the scrubbing zone the condensed heavy fractions being returned to the coking zone and there substantially completely converted to coke and lighter products. Accordingly, the invention is of particular value in 30 dual zone processes wherein vaporized petroleum stocks having high coke forming tendencies as indicated by Conradson carbon values between about 5 and 35, such as reduced crudes obtained by atmospheric or vacuum distillation and representing about the bottom 35 2 to 25 vol. % of the virgin crude distilled, are passed to a catalytic conversion zone. However, beside crude stocks, the invention may be applied to clarified cycle oil from catalytic cracking, to various pitches and tars from visbreaking operations.
- If desired, the oil feed or portions thereof 40 may be added at a low point in the coking bed while the rest of the feed may be added higher up. Thus, clarified oil represents a refractory stock which makes relatively high carbon in catalytic cracking, and which it is desired to destroy. This can best be accomplished by injecting it near the bottom of the coking bed. Heavy bottoms from the scrubber can be 45 handled in a similar manner.
- Prior to feeding to the first coking zone, the heavy feed stocks may be cut back with naphtha or other light products, and preferably preheated to temperatures ranging from 200 to 1000° F., or especially 600 to 800° F. Moreover, the hydrocarbon feed may also be diluted in either reaction zone with steam, recycle gas or other inert gas in amounts up to about 500 to 5000 cubic feet (at coker conditions) per barrel, since such diluent may often be necessary to raise the gas velocity to a proper level for fluidization of the beds of solid particles. Generally it is desirable to operate at linear superficial gas velocities 50 ranging from about 0.5 to 5 or 10 feet per second so as to establish apparent densities in the dense fluidized phase of about 10 to 50 lbs./cu.ft. and about 0.01 to 5 lbs./cu.ft. in the disperse phase thereabove, as is well known per se.
- The contact solids in the coking zone are preferably coke particles ranging in size up to about 500 microns, or preferably from 40 to 150 microns, though other finely divided, essentially inert solids such as sand, spent clay or pumice may similarly be used where a coke product of high inorganic ash content can be tolerated.
- The contact solids used in the catalytic cracking zone may be any finely divided cracking catalyst such as activated clays, activated alumina, synthetic composites of silica with about 5 to 50% alumina, or other conventional cracking catalysts such as those containing silica together with magnesia and/or boria. The solids in the cracking zone may also contain a conventional reforming catalyst such as activated carbon, clay or bauxite, whereby the octane number of the naphtha produced in the coker may be improved and higher boiling hydrocarbons cracked. The particle size of the cracking zone catalyst, as well as the apparent densities and superficial gas velocities prevailing in the cracking and regeneration zones are substantially within the same limits as given above with reference to the coker solids.
- When a catalytic cracking process is carried out in the second reaction zone the spent catalyst is preferably continuously renewed and passed to a regenerator wherein it is contacted as a fluidized bed with an oxygen containing gas to burn off the carbonaceous deposits and regenerate the catalyst at temperatures between 1000 and 1300° F. and preferably between 1100 and 1200° F.
- Reaction conditions may include temperatures in the first reaction zone of about 800 to 1200° F., preferably 850 to 1100° F., and temperatures of about 800 to 1200° F., preferably 950 to 1100° F., in the second for example catalyst cracking zone. Of course, the regeneration temperature must not be chosen so high as to cause serious deterioration of the catalyst being used, it being well known that 115 120 125 130

various catalysts cannot be heated above certain readily determinable temperatures without permanently reducing their catalytic activity.

- 5 In the first and second reaction zones the weight ratio of oil to total solids may be from about 0.1 to 5 lbs./lb./hr., and the oil vapors rising from the condensation zones into the second reaction zone preferably are characterized by a boiling range below about 950 to 1200° F. The ratio of coke to oil feed may be up to about 0.5 or 1.0 lbs./lb. Pressures in the coking and cracking zones may range between about 5 and 100 psig, although pressures in the lower part of this range will usually be used, especially in the regeneration zone.

Two embodiments of the present invention are illustrated by way of example in the accompanying drawings in which Figure 1 shows an apparatus suitable for the processing of a heavy petroleum residue by first subjecting the residue to a coking treatment in the presence of a finely divided inert solid and then subjecting the resulting products to a catalytic cracking treatment. Figure 2 shows an apparatus suitable for the processing of a similar heavy petroleum residue by first subjecting the residue to a continued coking and cracking treatment in the presence of a finely divided inert solid to produce products boiling in the gasoline range and subjecting these products to a further treatment in the presence of a finely divided catalyst.

In practicing the invention, according to the embodiment shown in Figure 1, a residual petroleum stock such as a reduced crude having a gravity of about 5° API is passed through line 201 to a suitable heat exchanger 202 which, in this instance, is a coil immersed in the hot fluidized catalyst bed in a regenerator vessel 203. On passing through heat exchanger 202, the feed gets preheated to a temperature between about 400 and 1000° F., preferably between 600 and 700° F. The most desirable preheat temperature will depend upon various heat balance considerations, as will be discussed later. The preheated liquid feed from coil 202 and/or other feed introduced at point 201a is introduced through line 204 into the dense fluidized coke bed 205 where it is vaporized and partially coked.

The actual feed introduction to bed 205 can be carried out in several ways. For instance, spray nozzles 209 may be evenly spaced across a horizontal cross-section of the coker on a series of straight or circular manifolds, either in a single horizontal plane or in a plurality of vertically spaced planes, so as to give a shower or liquid curtain extending horizontally across substantially the entire vessel. With such an arrangement, some advantage may be obtained even in the absence of illustrated trays 211 and 213 by keeping valves 207 and 208 closed and by delivering the liquid feed from line 204 to bed 205 directly through the spray nozzles

209, provided that the nozzles are located a substantial distance, e.g. 10 to 20 feet, above the dense bed level 218 so as to cause effective scrubbing of the vapors. In such a case, the feed vapors produced by contact with the hot solids in bed 205 pass countercurrently through the shower of relatively cool, descending feed so that entrained coke fines are scrubbed out and the heaviest components of the rising vapors are condensed and refluxed to coking bed 205. However, such spray scrubbing of the vapors is often only incomplete, may result in entrainment of droplets of undesirably heavy components of the feed into the catalytic cracking zone, and therefore does not represent a preferred embodiment of the invention. Also less uniform feed distribution in the coke bed is obtained when the feed nozzles are high above the bed level.

Consequently, in the preferred embodiment of the invention, valve 206 is closed and the partially preheated feed is introduced through open valve 207 and line 210 onto liquid contacting perforated plate 211 and then to perforated plate 213, so that the feed may pick up further preheat before entering the coker. The liquid hydrocarbon pools on plates 211 and 213 may be maintained between about 600 to 1000° F., but preferably below 850° F. to avoid undue coking, and act as a scrubber for the hot vapors ascending from coking bed 205 to the cracking zone 220. Thus the heavy, coke-forming ends are effectively removed by partial condensation of the vapors while entrained dust is also removed from the rising stream.

From plate 211 the liquid mixture which in the absence of lower plate 213 contains feed, heavy condensate and slurred solids entrained in the gases from the first reaction zone may be caused to overflow directly into coker bed 205 maintained at about 850 to 1100° F. Preferably one or more lower plates 213 are provided in which case the liquid on plate 211 is passed through downcomer 212 onto one or more lower plates 213 before being pumped through line 214, valve 208 and distributive spray nozzles 209, into the coking zone 205. In this arrangement the solids in the vapors from the coking zone will be retained in the liquid on the lower plate 213. Unlike in the alternative embodiment mentioned above, here nozzles 209 need not be spaced across the entire cross-section if the vessel, since it is not among their primary functions to produce a spray for scrubbing the ascending vapors. However, even here uniform feed distribution is desirable. A portion of the effluent from lower plate 213 may be recycled through line 215 and cooler 216 onto the upper plate 211, in order to control the temperatures of the scrubbing plates. If desired, a slurry settler 221 or an equivalent separation device such as a filter may also be connected to line 214 so as to prevent build up of coke fines in the

scrubbing section.

Coking zone 205 is partially filled with finely divided coke ranging in size between 40 and 150 microns through which an aeration gas such as steam from line 217 is passed in an upward direction to produce a total superficial vapor velocity of about 1.5 to 3 feet per second, thereby maintaining the solids in the form of a dense fluidized bed having a density of about 20 to 40 lbs./cu.ft. and having an upper level 218 above which extends a more dilute phase having a density of only about 0.01 to 1 lb./cu.ft. The fluidized solids in zone 205 may amount to about 0.1 to 5 lbs. per lb. per hour of injected hydrocarbon feed and are maintained at a temperature of about 800 to 1200° F., the temperature preferably being such that the heavy constituents of the hydrocarbon feed are converted to a solid carbonaceous residue or "coke," without, however, converting any substantial fraction of the feed into naphtha or gasoline type products. Generally the residence time of the hydrocarbon vapors in the coking bed 205 may range from about 3 to 25 seconds before passing in rapid succession through scrubber plates 213 and 211 and through perforated plates 219 into catalytic cracking bed 220. Net coke product may be withdrawn from bed 205 through line 222. Also, some of the withdrawn coke may be recycled to coke bed 205 after passage through a grinder or other size reducing device, thereby maintaining the particle size distribution of the coke in the cracking zone within a range suitable for proper fluidization.

The major importance of the present invention lies in the fact that it allows easy removal both of coke fines and of high coke-forming heavy ends from the coker vapors ahead of the catalytic cracking step where these constituents would rapidly contaminate the catalyst and thus put an undue load on the regeneration system. Specifically, as the vapors ascending from coking bed 205 pass through the liquid on the contacting plate 213, entrained coke dust is scrubbed out and the resulting suspension or slurry of coke in liquid feed is returned to coke bed 205 through line 214 and sprays 209. Moreover, it must be noted that the advantages of the present invention can also be substantially realized in cases where it may be desirable to add part or all of the oil at a lower point in bed 205. For example, oil may be delivered via line 217, with or without the addition of the recycle solids from line 222. This contributes to aeration of the bed in zone 205, while liquid for the scrubbing plates may be obtained by an increased rate of recycling of oil through lines 214 and 215 and water cooler 216 to upper plate 211.

Where more than one scrubber plate is used as illustrated, it is preferred to maintain the temperature on the bottom plate 213 in a range between about 750 or 850° F. and the

temperature of the coking zone, so that entrained solids are scrubbed out, but relatively little condensation of the passing vapors, and also only a minimum of further coking, occurs thereon. The vapors scrubbed on plate 213 then rise up and through an upper contact plate 211 which is maintained at a lower temperature, between about 600 and 800° F. so that the heavy ends, which would otherwise result in extremely high carbon yields on catalytic cracking, are removed from the ascending vapors by partial condensation. In this manner, most of the scrubbing is effected on the upper plate at a relatively low temperature which minimizes coking, while the gradient between the plates facilitates preheating the incoming feed to a high degree.

Relatively high temperatures may be used to limit the extent of condensation from the coker overhead vapors, and also to give high preheat to the oil flowing through the scrubber. Contact time of the oil can be minimized so as to avoid excessive cracking and coke deposition in the scrubbing system. The presence of solids in the oil also helps to prevent difficulties due to coke deposition. Operation of the scrubber at lower temperatures will give more condensation of heavy ends from the coker overhead. Thus operating conditions in the scrubber can be regulated to give the optimum balance between the components going to catalytic cracking and the heavy ends which are recycled to the coking section or withdrawn from the system.

In some cases it may be preferable to use a scrubbing oil other than fresh oil feed. For example, this may be a heavy extraneous oil or, as previously mentioned, may consist simply of the heavy ends which are condensed out of the coker overhead and then recycled, preferably after clarification thereof in slurry settler 221 and cooling in exchanger 216 to give the required temperature control.

Solids loading in the slurry should be controlled within the range of about 0.1 to 1.0 lbs./gal. in order to avoid any tendency to plug the equipment. Also, it is possible to add cyclones between the coking and scrubbing sections in order to reduce solids carryover. In some cases, particularly where entrainment is high, as due to high velocity operation, this may be very desirable, if not essential, but usually will be unnecessary where the liquid spray is properly distributed across the entire vessel.

As indicated earlier, the scrubbing plate may serve as an inexpensive means for preheating the feed, and it will be understood, of course, that fresh feed may be introduced directly onto lower plate 213 rather than upper plate 211 as shown in the drawing. Also, it will be understood that a system containing a greater number of scrubbing plates can be used instead of the two plates illustrated; or, alternatively, the advantages of the invention can be

- achieved at least to some extent even when only a single scrubbing plate is used, serving the dual purpose of removing coke fines and partially condensing the heavy, coke-forming vapor constituents.
- The considerations involved in the selection of operating temperature in the scrubber will now be discussed in greater detail. A major factor is that the scrubbing should be such as to give the desired cut point on the coker overhead, so as to exclude undesirable heavy ends from the cracking zone. This cut point should be such as to give the best over-all process, and balance the relative conversions in the coking and cracking zones. The cut point given by the scrubber will depend upon temperature, pressure, amount of gas and vapors flowing, characteristics of the scrubbing oil, and number of scrubbing plates. From these, the operating temperature may be calculated using the usual engineering procedures. Having determined the proper scrubbing temperature, the equipment is then designed to meet the required heat balance. The latter may preclude passing all of the feed through the scrubber if insufficient heat is available. This may affect the desired preheat which must be obtained in preheat coil 202 or equivalent preheat furnace. Similar considerations will show whether it is necessary to include a heat exchanger on a recycle oil stream.
- The characteristics of the feed and other conditions may make it advantageous to use an extraneous oil for scrubbing. Oil from the scrubbing section can be withdrawn from the system and may constitute one of the product fractions.
- From contacting plate 211 the hydrocarbon vapors rise through perforated distributor plate 219 into a cracking zone wherein finely divided cracking catalyst such as activated clay or a silica-alumina composite is maintained as a dense fluidized bed 220 by the upward passage of the vapors therethrough. The diameter of the cracking zone which contains catalyst bed 220 is greater than the diameter of the underlying coking zone to prevent excessive vapor velocities in catalyst bed 220, which otherwise may result from the increase in total vapor volume during catalytic conversion. The cracked hydrocarbon vapors together with inert gas introduced into the lower coking bed 205 are withdrawn from the cracking zone through cyclone 223 and passed through line 224 to a conventional fractionation system for recovery. The contact time of the vapors in cracking zone 220 may range from about 10 to 30 seconds at about 800 to 1200° F., the vapor velocity, fluidized bed depth and apparent density of the dense phase being in the same range as in the earlier described coking zone. Entrained catalyst fines are separated from the cracked vapors in cyclone 223 and returned to the cracking zone through dip leg 225 which extends below the upper level 226 of the dense fluidized catalyst bed 220.
- Spent catalyst may be withdrawn from catalyst bed 220 through standpipe 227, which may be provided with one or more taps 231 for admission of minor amounts of an aeration gas, and is hydraulically lifted into regenerator vessel 203 by means of an oxygen-containing gas such as air injected into the withdrawn catalyst through line 228. Above the perforated distributor plate 229 in regenerator 203 the catalyst is again maintained as a dense fluidized bed having an upper level 230 while the carbonaceous deposit is burned off the catalyst at a temperature of about 1050 to 1250° F. in a manner well known *per se*. Low regenerator pressures in the neighbourhood of about 1 psig. are preferred so as to save on air compression costs, but where desired the combustion may be carried out at other pressures which may range from 1 to 25 psig. The flue gas produced in the regenerator is removed overhead through entrainment separator 232 and line 233 while the recovered catalyst fines are preferably returned to the dense bed in the regeneration zone.
- Hot regenerated catalyst is recycled from regenerator 203 to the dense catalyst bed 220 in the cracking zone, thereby keeping the activity of the catalyst at a relatively high level and also supplying the necessary sensible heat and heat of reaction to the cracking zone. Thus, regenerated catalyst may be returned to the cracking reactor through line 234. However, since the feed to the cracking zone consists of vapors at high temperature, the sensible heat requirement for cracking is usually small, making excess regeneration heat available in other parts of the process. For instance, it may be desirable to construct line 234 in indirect heat exchange with a feed pre-heater or a steam generator 245 to remove some heat from the catalyst returning to the reactor. This permits operating at higher catalyst to oil ratios in the cracking step than would be possible with uncooled regenerated catalyst. Some of the hot regenerated catalyst may also be aerated and circulated from regenerator 203 through line 235 to indirect heat exchanger 236 which is submerged in the fluidized bed 205, thereby supplying the required coking heat or heat may be exchanged directly by mixing coke and catalyst of different size and separating the catalyst from the resulting mixture by elutriation. Alternatively or additionally, excess heat may be used for other purposes such as product reboiling or steam generation. For example, a water coil may be immersed in hot fluidized catalyst either directly in the regenerator bed or in a separate vessel through which hot catalyst is circulated either from the reactor or the regenerator.
- Of course, where none of the regeneration heat is transferred to the coking zone, other means must be used for supplying the neces-

sary heat to the coking zone. For example, such heat may be obtained by withdrawing a portion of the coke from fluidized bed 205 through standpipe 239 and burning a portion of the withdrawn coke in transfer line 240 after mixing with air admitted through line 241a. If desired heat can also be supplied by contacting the coke with hot flue gases, formed by combustion under controlled conditions in an auxiliary burning zone as disclosed in our pending Application No. 13677/52 (Serial No. 714,210). the heated coke is then separated from the flue gases in entrainment separator 241b and returned to coke bed 205 through leg 242 provided with aeration taps 243. Where desired, a portion of the hot coke from separator 241b may also be branched off through standpipe 244 and mixed into fresh feed so as to preheat the latter, and to control coke accumulation in the preheat circuit. Regardless whether all of the hot coke from separator 241 is returned directly to coke bed 205 or whether some of it is added to the feed, a substantial advantage is obtained by this use of the transfer line coke heater. Moreover where partial combustion of the coke in the transfer line is feasible, there is also the advantage that this increases the surface area of the circulating coke so that improved coking is obtained in the coking zone.

The physical arrangement of the apparatus illustrated may be modified in various ways. For example while the feed preheater coil 202 is shown wholly submerged below the catalyst level 230 in the regenerator, it is possible to vary the catalyst level so as to expose more or less of the heat exchanger surface above the level, thereby controlling the degree to which the liquid feed is preheated. Also, while the heat exchanger 236 within the coker has been schematically illustrated as a coil, a shell-and-tube type heat exchanger or any other heat exchanger of suitable design may be used likewise. Moreover, while the feed is shown to be first preheated in the regenerator coil 202, a preheat furnace may be used; or it is entirely feasible to introduce cold feed directly onto plate 211 where it can be preheated by the hot vapors rising through it; or the feed, cold or preheated, may be introduced directly onto lower plate 213.

Referring now to Figure 2, the reference character 10 designates a vessel having a cracking or coking section 12 in its lower portion, two scrubbing sections 14 and 16 higher up in the vessel and a treating section 18 near the top thereof. The coking section 12 is provided with a dry dense fluidized highly turbulent bed 22 of inert finely divided solid particles which may be sand, coke, pumice, Kieselguhr, carborundum, alumina, spent clay catalyst or spent synthetic silica-alumina catalyst, but preferably is petroleum coke. Coke is formed during the coking or conversion of the heavy residual oil in fluidized bed

22 and either deposits on the inert solids or forms additional coke particles. A part of the coke so formed is burned to supply heat for the conversion of the heavy residual oil as will be hereinafter described. The finely divided solid particles preferably have a size between about 30 and 200 standard mesh or finer and the density of the fluidized bed 22 is between about 15 and 45 pounds per cu. ft. The superficial velocity of the gases and vapors passing upwardly through the bed 22 to maintain the particles in dense fluidized condition is about 0.1 to 5.0 feet per second. The fluidized bed 22 has a level indicated at 24. Excess coke is withdrawn from bed 22 through line 25.

The heavy residual petroleum oil to be cracked or converted may have an API gravity of 20° or lower, Conradson carbon between about 5 and 35% wt., and an initial boiling point of about 1000° F. or higher. The feed may include such materials as catalytic or thermal cracked bottoms or cycle oil, visbreaker tar, asphalt, or tar from coking. It may also contain fractions boiling lower than 1000° F., if desired. The heavy residual oil is passed through line 26 and for preheating may be passed through coil 28 entirely or partially submerged in dense fluidized bed 32 of retreating catalyst in regeneration zone 34. The residual oil feed may bypass the coil 28 through bypass line 36 and pass through line 38 and valved line 42 to line 44 and nozzles or spray devices 46 arranged above level 24 of coking bed 22 to discharge the residual oil onto the coking bed 22. If desired, the residual oil for additional or initial preheating may be passed from line 38 through line 48 and heating coil 52 partially or completely submerged in the slurry layer 54 in scrubbing zone 16 and then through heating coil 56 partially or completely submerged in slurry 58 in lower scrubbing zone 14 in vessel 10. The preheated residuum at a temperature of about 600° F. to 1000° F. is passed through line 44 and into coking bed 22. It will frequently be preferable to introduce part or all of the oil feed at the bottom of bed 22, and by line 84, in order to effect better contacting and give higher conversion. Also a distribution grid may be included at the inlet.

For supplying heat to the coking bed 22 in the coking zone, some of the coke particles or coke-containing particles are withdrawn from the dense fluidized bed 22 through standpipe 62 having a valve 64 at its lower end for controlling the rate of flow of solid particles through standpipe 62. Air or other oxidizing gas is introduced through line 66 and picks up the withdrawn solid particles as a suspension which is passed through transfer line burner 68. In the transfer line burner the velocity of the combustion gases is between about 5 and 75 feet per second and the density of the suspension passing through transfer line burner 68 is about 0.1 to 3 lbs. per cu. ft. The tem-

- perature of the solid particles in burner 68 is about 1000° F. or higher. If preferred, the solids leaving line 64 may be heated by contacting them with hot flue gases from an auxiliary burning zone. 5
- The combustion gases and suspended coke and/or other solids are passed to a gas-solids separating device such as a cyclone separator 72, the separated hot combustion gases passing overhead through outlet line 74 and thence through a heat exchanger such as a waste heat boiler (not shown), if desired. The separated heated solid coke or other particles are passed to standpipe 76 having a control valve 78 at its lower end for controlling the rate of withdrawal of solids from the separator 72. The withdrawn heated solids are picked up by steam or other suitable gas introduced through line 82, and the solid particles at a temperature of about 900° to 1800° F. are passed through line 84 as a suspension and into the bottom portion of the coking or conversion zone comprising fluidized coking bed 22. The steam or other gas introduced through line 82 assists in fluidizing the bed 22 of solids in the coking zone in the bottom of vessel 10. 10
- As an alternate some of the residual oil pre-heated or not may be passed from line 38 through alternate line 86 for admixture with the heated solid particles withdrawn from standpipe 76 and then passage through line 84 to cause conversion of the heavy residual oil by mixing the oil with solid particles heated to a much higher temperature than that which exists in coking bed 22. For example, this line 84 may be operated at say 200° F. higher than reactor temperature and since the contact time is low, cracking will not be excessive. Also, selected feed fractions such as bottoms from catalytic treating or cracking or scrubber slurry from line 124, or 116, can be added preferentially to line 84 through line 87. In this form of the invention steam is also added through line 82. 15
- In the coking zone 22 the temperature is maintained at a temperature between about 900° and 1300° F., the pressure is between about atmospheric and 200 lbs. per sq. in. gage and the residence time of the vapors in coking zone 22 is about 4 to 100 second. During coking, gas, gasoline, gas oil and higher oils and coke are formed and at high coking temperature the gasoline formed has undesirable high gum but is of high octane number. Also during coking with the temperature as high as these, high boiling hydrocarbons are vaporized so that the vapor products leaving coking bed 22 contain high boiling products which must be separated from the product gasoline. The vapor products leaving coking bed 22 contain entrained coke also. To remove the high boiling constituents and coke particles from the vapor products leaving the coking bed 22, the vapors may be passed through perforated scrubbing plate on which the slurry 58 is located. The slurry 58 will usually be maintained at a lower temperature than the coking or conversion temperature and the temperature is between 300 and 850° F., preferably 600—800° F. The slurry is maintained at the lower temperature by coil 56 previously referred to as being used for preheating the residual oil feed, if desired. Additional cooling is obtained by cooler liquid flowing down onto scrubbing plate 88 from the upper scrubbing zone 16 via downcomer 57. 20
- The cooling for the slurries in scrubbing zones 14 and 16 will now be further described. The upper slurry 54 of heavy ends or higher boiling constituents on upper scrubbing plate 92 is partly cooled by indirect heat exchange with residual oil feed passing through coil 52 as above described. For maintaining the temperatures of the slurries 58 and 54 on plates 88 and 92 at the desired levels, oil slurry containing heavy ends and coke particles is withdrawn from scrubbing plate 88 through line 94 and passed through cooler 96 and thence through lines 98 and 102 to the slurry 54 on top scrubbing plate 92. While two scrubbing plates 88 and 92 have been shown, it is to be understood that only one such plate may be used. The temperature of scrubbing oil or slurry 54 on top scrubbing plate 92 is maintained between about 300° F. and 800° F., but will generally be less than slurry 58 on plate 88. 25
- Instead of returning all the slurry to top scrubbing plate 92, a part thereof may be passed through line 104 to separator 106 for separating solids from liquid. The separator 106 is preferably a settler or thickener to concentrate the solids in liquid and the more concentrated slurry may be withdrawn from settler 106 through line 108 and returned to the coking bed 22 through line 112 having nozzles or spray members arranged above the level 24 of dense bed 22. Or the concentrated slurry may be withdrawn from the system through line 116 to reject fines from the coking system. In some cases it will be desirable to use cyclones above bed 22 to limit the amount of solids carried up to the scrubbing zone. 30
- The cooled and clarified oil or oil containing less suspended solids than the slurry 54 on plate 88 is withdrawn from the upper portion of settler 106 through line 118 and passed through line 122 and then 102 for return to upper slurry 54 on top scrubbing plate 92. Or some of the clarified oil may be withdrawn from the system through line 124 to offset the oil recovered by condensation from the vapors entering from bed 22. This heavy oil may constitute one of the product streams or it may be recycled to bed 22 via line 84. Extraneous oil such as feed may be added at 35
103. The slurry temperature in line 102 may be controlled by adding the cool make-up oil feed through line 103. The latter may contain light components which are stripped out on 40
- 105
- 110
- 115
- 120
- 125
- 130

- plates 92 and 88, and are carried up to treating zone 18. In some cases, it will be desirable to operate scrubbing sections 14 and 16 separately and with independent cooling and oil withdrawal systems. Several plates may be used in each section to separate different product fractions.
- As the vaporous products at a relatively high temperature or coking bed temperature leave the coking bed and are first scrubbed with residual oil feed from sprays 46 and cooled recycle oil from sprays 114, this removes some of the extremely high boiling materials carried as vapors in the products leaving the coking bed. The vapors at a temperature between about 800° and 1100° F. pass upwardly through perforated scrubbing plate 88 and there intimately contact the oil slurry 58 maintained at a lower temperature to condense higher boiling constituents from the product vapors and also to scrub out any entrained coke particles.
- The vapors then leave scrubbing zone 14 at a temperature of about 300° F. to 800° F. and pass through top scrubbing plate 92 in the scrubbing zone 16 for intimate contact with the oil slurry 54 maintained at a lower temperature than scrubbing zone 14 to condense constituents higher boiling than gasoline so that the vapors leaving upper scrubbing zone 16 are substantially gasoline vapors to be treated in the gasoline treating section 18 which comprises a perforated plate or tray 128 supporting a dry fluidized bed 132 of finely divided clay or other treating catalyst having a level indicated at 134. Instead of a fluid bed a fixed bed of catalyst may be used. The treating catalyst is preferably in finely divided form between about 30 and 200 standard mesh or finer with most of the particles being between about 40 and 150 microns. The velocity of the upflowing vapors through treating zone 18 is selected to maintain the finely divided catalyst particles as a dense fluidized highly turbulent liquid-simulating bed having a density between about 20 and 45 lbs. per cu. ft.
- As a treating catalyst, bauxite or clay, spent or used silica alumina synthetic cracking catalyst, silica gel adsorbent, char or activated carbon may be used. Treating may be carried out using catalysts activated with chromium, molybdenum, or phosphoric acid. As pointed out above, coke is formed during the coking operation and this coke may be used as a starting product for making a treating catalyst. For example, excess coke may be withdrawn from coking bed 22 through line 25 and ground to the desired size and then treated with steam and/or air at a temperature of about 1600° to 1800° F. to give 50 to 80% yield of activated char or carbon. Similar conditions may be used for revivifying used treating solids.
- An indirect heat exchanger 136 may be partially or completely submerged in fluidized bed 132 in the treating zone 18 for maintaining the temperature of the treating fluidized bed 132 between about 500° and 900° F. with a solids hold up on plate 128 to give 1 to 10 parts by weight of oil vapors treated per hour per weight of solid. The heat exchanger 136 is used to add heat or remove some heat of reaction from the treating zone 18. If desired, direct heat exchange may be used in treating zone 18.
- Treated vapors leaving dense fluidized bed 132 in treating zone 18 pass to dilute phase above the dense bed and contain entrained catalyst particles, so the vapors are passed through a gas-solids separating device 142 such as cyclone separator for separating entrained solids. Separating device 142 is located in the upper portion of vessel 10. The vapors pass overhead through line 144 and are handled as desired to recover treated gasoline which is of improved quality from the standpoint of gum, sulfur, octane number, or lead susceptibility. The separated solids are passed to dip pipe 146 and returned to the dense bed 132 in treating zone 18 below the level 134.
- With some treating catalysts such as cracking type catalysts or other inorganic catalysts such as silica or alumina base types the coke which deposits on the catalyst may be removed by burning with air and the heated regenerated solids then returned to the treating zone, any excess heat being transferred to oil feed or product streams or being utilized to produce steam. Carbonaceous type treating agents may be revivified as above stated with steam and/or air under controlled conditions.
- The catalyst from the treating zone to be regenerated is withdrawn through line or standpipe 148 having a control valve 152 at its lower end. Air or other regenerating gas introduced through line 154 picks up the withdrawn catalyst and the mixture as a dilute suspension is passed through line 156 to the lower portion of regeneration vessel 34 below distribution grid 158 therein. The velocity of the gases passing upwardly through the regeneration vessel is selected to be between about 0.5 and 5.0 ft. per second to produce dry dense fluidized bed 32 of solids above referred to. The bed 32 has a level indicated at 162 with a dilute phase 164 thereabove.
- The gases leaving the dense bed contain entrained catalyst particles which are mostly removed by passing the gases through a gas-solids separating device 165 arranged in the upper portion of the regeneration vessel 34. The combustion gases pass overhead from line 166 and may be passed through a waste heat boiler to recover heat therefrom. The separated solids are returned through dip pipe 168 to the dense fluidized bed 32 below the level 162 thereof. Any excess heat of regeneration may be removed by a heat exchange coil 172 partially or completely submerged in dense fluidized

- bed 32. Hot regenerated catalyst passes from the dense fluidized bed 32 into well 174 and thence to standpipe 176 having a control valve 178 at its lower end for controlling the amount of regenerated catalyst passing to the dense fluidized treating bed 132 in treating zone 18.
- During regeneration the temperature is maintained between about 900° and 1250° F. and regenerated catalyst at this temperature, or cooled to a lower temperature, is returned via standpipe 176 to treating section 18. Heat from regeneration vessel 34 may also be used in the coking bed 22 using indirect heat exchange as discussed in connection with coil 28. Heat exchange may also be effected by circulating hot catalyst in indirect exchange with coke from bed 22. In some cases the hot catalyst may be contacted directly with the coke and then separated by elutriation, with the catalyst returned to the catalytic section and the coke returned to the coking section.
- While the heavy residual oil is shown as being introduced above the bed 22 and into the bottom portion of the bed 22, it may also be introduced directly into the bed 22 at intermediate points.
- The slurry on plates 88 and 92 functions as a partial condenser, that is, partial condensation of highest boiling constituents takes place so that the end point of the distillate going to the treating zone 18 is controlled, for example, to the gasoline end point of roughly 400° F., but may extend up to 600° F.
- EXAMPLE.**
- As an example of our invention, its application to the treating of naphtha from a high temperature coking operation is described. Residuum of about 7° API gravity and 20% Conradson carbon is fed to the unit shown in Figure 2, as described previously. The coking zone is maintained at 1100° F., and without our treating step the 30 vol. % yield of C₆/430 naphtha would have high sulfur, poor stability, short breakdown time, and very poor engine cleanliness characteristics. Conjugated diolefins are present to the extent of up to 15% of the total naphtha, and cyclic olefins to about 10—15%.
- In our process, the total overhead from the 1100° coker zone is run through a fluidized bed of silica-alumina cracking catalyst maintained in the range of 700° to 775° F., preferably at about 750° F. The temperature of the scrubbing plates is maintained to keep material of a normal boiling point higher than 600° F. from entering the treating bed, and most of the material passing through the plates boils below 450° F. In this instance the medium gas oil is removed via the scrubbing oil, although treatment of this fraction also is possible by raising the scrubbing temperature.
- The weight of material processed per hour is in the range of 0.1 to 1.0 times the weight of catalyst in the bed, preferably about 0.3 to 0.5. At higher temperatures, higher rates may be used. Some carbon may be deposited, in this case about 1%, and the catalyst is regenerated to maintain activity. Catalyst to material processed weight ratio may range from 0.5 to 20, but in this case a ratio of 2 to 5 is sufficient.
- The gasoline resulting from this treatment will have the conjugated diolefins and cyclic olefins reduced to about 1 to 5% and cleanliness characteristics, stability and breakdown time will be much improved. A striking demonstration of the improvement obtained is that this naphtha will remain water white or nearly so indefinitely; naphtha directly from the 1100° coking bed turns very dark within 24 hours.
- In this combination process, coking, scrubbing and treating steps have been combined with a saving in equipment and with a high level of heat economy. At the same time, a wide range of flexibility in possible operating conditions for each step has been maintained, and operability of the system has not been impaired. Moreover, it provides a combination process wherein the treating catalyst can be kept entirely separate from the coke, so that valuable catalyst is not lost as a result of sticking with coke in the coking zone, nor is the catalyst contaminated by entrainment of coke into the treating zone. In addition, heavier components of the vapor from coking can be excluded from the treating zone where they might tend to result in excessive coke deposits and product degradation.
- Where treating zone 132 of Figure 2 is operated as a catalytic cracking zone, a further catalytic up-grading treatment may be provided by locating a further bed of suitable catalyst above zone 132, one or more scrubbing zones being provided above zone 132 so that cracking vapors therefrom pass through the scrubbing zones and undergo removal of higher boiling constituents before being passed to the final treating bed. In this case the final treating bed would be operated at about 600—850° F. and the catalytic cracking zone at a temperature of about 800—1000° F.
- What we claim is:—
1. A method of converting a heavy hydrocarbon feed, such as a heavy petroleum residuum oil, into lighter fractions which comprises subjecting said feed to a thermal cracking and coking treatment in a first reaction zone in the presence of inert finely divided solids, passing the product vapors from said first reaction zone through a scrubbing zone in which they are scrubbed by a liquid hydrocarbon oil which serves to condense and retain in the scrubbing zone the higher boiling constituents of said product vapors and any finely divided solids entrained therein, passing the vaporous effluent from the scrubbing zone to a second reaction zone wherein said vaporous effluent is subjected to a catalytic up-grading

treatment in the presence of catalytically active solids, and removing up-graded hydrocarbon vapors from said catalytic conversion zone.

5 2. A method according to Claim 1, wherein the scrubbing zone contains a pool of said liquid hydrocarbon oil through which the product vapors from the first reaction zone are passed.

10 3. A method according to Claim 2, wherein the solids in said first and second reaction zones are maintained in the form of dense turbulent fluidized beds of finely divided solids and wherein the second reaction zone is located vertically above the first reaction zone, the scrubbing zone being located between the two reaction zones and serving to retain therein finely divided solids entrained overhead from said first reaction zone whereby a slurry is formed in said scrubbing zone.

15 4. A method as claimed in Claim 2 or 3, wherein the pool of oil or slurry in said scrubbing zone is maintained at a temperature below that of said first reaction zone by removing at least a portion of the oil or slurry therein, and cooling and recycling same to the scrubbing zone.

20 5. A method as claimed in Claim 2 or 3, wherein the pool of oil or slurry in said scrubbing zone is cooled by the addition of cool make-up oil feed.

25 6. A method as claimed in any one of Claims 1—4, wherein oil or slurry is removed from said scrubbing zone and is passed to said first reaction with or without cooling.

30 7. A method as claimed in Claims 3 and 6, wherein the slurry removed from said scrubbing zone is passed to a settler to separate the solids from the oil and part of the clarified oil is passed to the first reaction zone and part is cooled and returned to the scrubbing zone to control the temperature thereof.

35 8. A method as claimed in Claim 7, wherein the slurry or clarified oil from the scrubbing zone is mixed with finely divided solid particles heated to a temperature above that prevailing in said first reaction zone before passing thereto.

40 9. A method as claimed in any one of Claims 3 to 8, wherein a further partial scrubbing zone containing a liquid pool of hydrocarbon oil is arranged above said aforementioned scrubbing zone and below said second reaction zone and the vapors leaving the said aforementioned scrubbing zone are passed through the pool of oil in said further scrubbing zone to effect a further removal of higher boiling constituents before passing to said second reaction zone.

45 10. A method as claimed in Claim 9, wherein the pool of oil maintained in said further scrubbing zone is hydrocarbon feed oil, which is preheated therein.

50 11. A method as claimed in Claim 9, wherein oil containing condensed hydrocarbons

is continuously removed from said further scrubbing zone and passed to the other scrubbing zone.

55 12. A method as claimed in any one of Claims 9—11 as appendant to Claim 7, wherein the cooled clarified oil is recycled to said further scrubbing zone.

60 13. A method as claimed in Claim 1, wherein the vapors and entrained solids from the said first reaction zone are passed through a gas solids separator to remove entrained solids before passage of the vapours to said scrubbing zone.

65 14. A method as claimed in any one of Claims 1—13; wherein the condensate condensed in said scrubbing zone or zones contains constituents resistant to cracking.

70 15. A method as claimed in any one of Claims 2—14, wherein the pools of liquid oil in said scrubbing zone or zones are also cooled by passing the hydrocarbon feed to the said first reaction zone in indirect heat exchange with the liquids in said pools.

75 16. A method as claimed in any one of Claims 1—15; wherein the vaporous effluent fed to said second reaction zone contains a substantial amount of a gas oil-boiling range fraction and the up-grading treatment in said second reaction zone is a catalytic cracking treatment.

80 17. A method as claimed in any one of Claims 1—15 wherein vaporous effluent fed to said second reaction zone contains a substantial amount of a gasoline-boiling range fraction which is subjected to a catalytic reforming treatment in said second reaction zone.

85 18. A method as claimed in Claim 17, wherein the scrubbing zone or zones are maintained at a suitable temperature to remove all constituents boiling above the gasoline range from the effluent vapors passed to the second reaction zone.

90 19. A method as claimed in any one of the preceding claims, wherein the finely divided solid in the first reaction zone is finely divided seed coke.

95 20. A method as claimed in any one of the preceding claims, wherein the heat required in said first reaction zone is produced by removing part of the coke-bearing solids therein and subjecting them to a combustion reaction to burn off some of the carbon and leave a highly heated residue, said highly heated residue being then returned to the first reaction zone.

100 21. A method as claimed in any one of the preceding claims, wherein the temperature in the first reaction zone is above 800° F. and preferably between 800 and 1200° F.

105 22. A method as claimed in Claims 9 and 21, wherein the further scrubbing zone is maintained at a temperature between 300 and 850° F. and the other scrubbing zone is maintained at a temperature below 1000° F. but above that of said further scrubbing zone.

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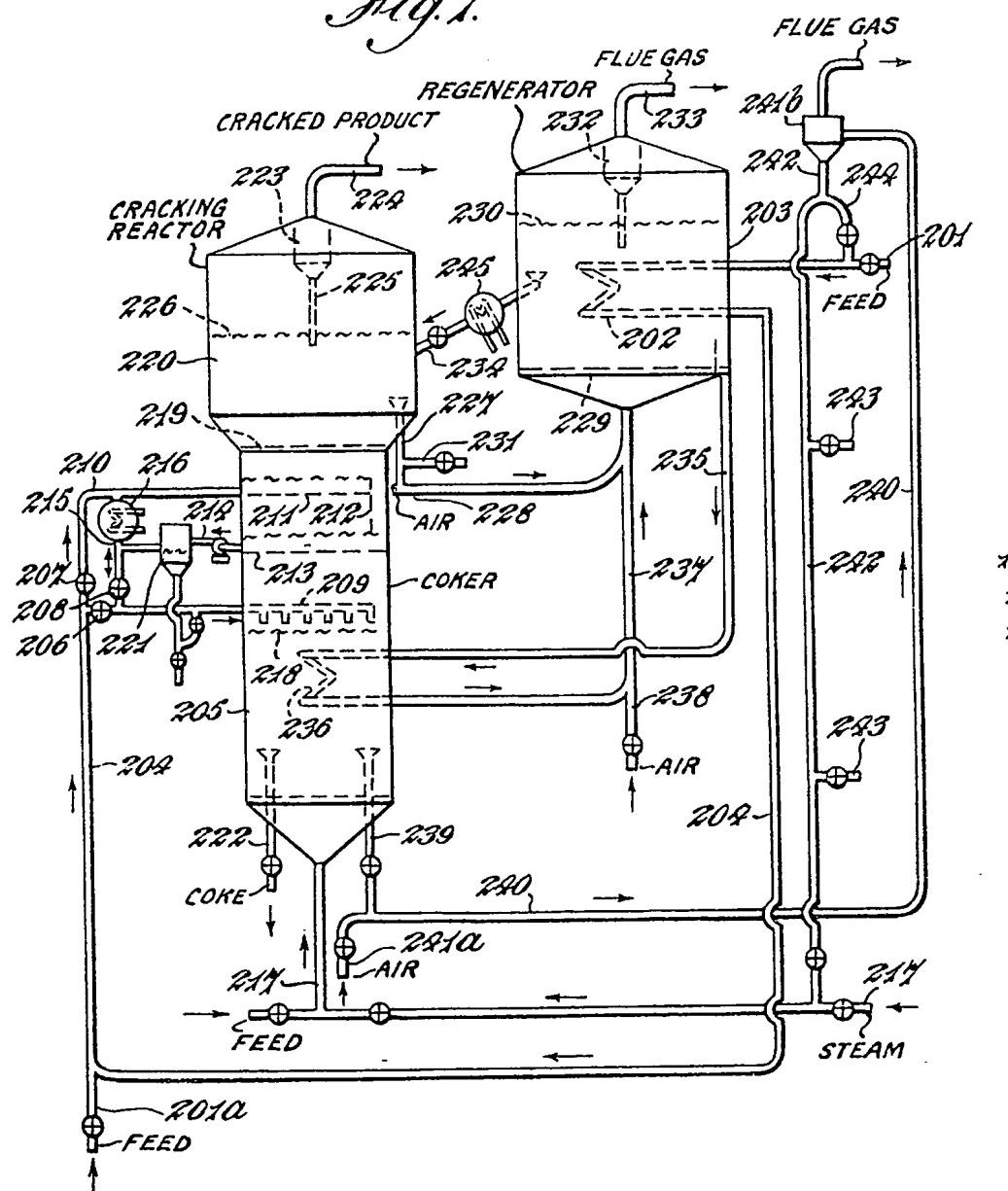
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23. The improved method of treating hydrocarbons substantially as hereinbefore described with reference to either of the Figures of the accompanying drawings.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1955.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

Fig. 1.

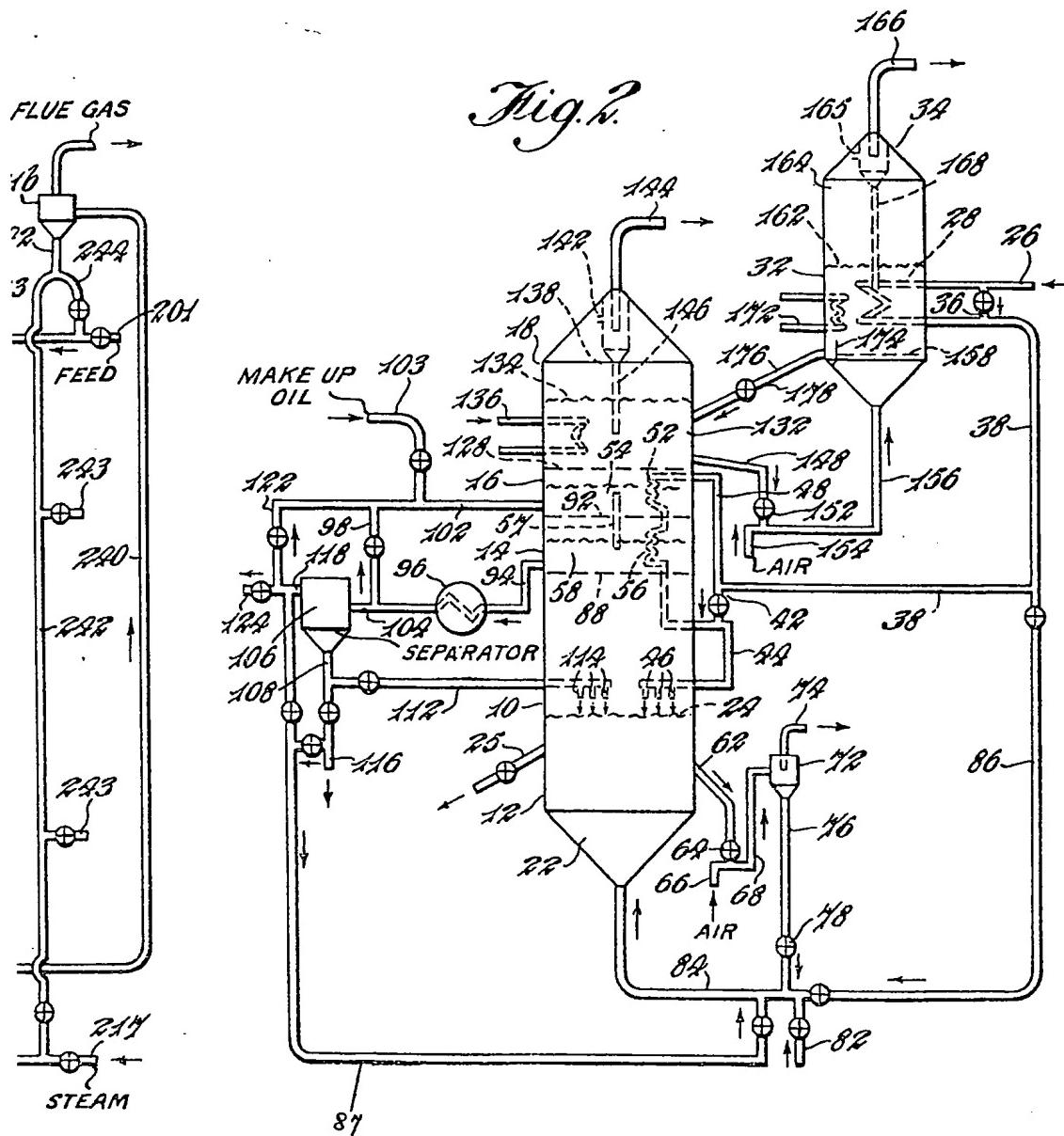


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